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U.S. DEPARTMENT OF ENERGY

First-principles Modeling and Design of Solid-State Interfaces for the Protection and Use of Lithium Metal Anodes

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Project ID: bat373

Overview

Timeline

- Start date: April 1, 2017
- End date: June 30, 2020
- Percent complete: 70%

Barriers

- Barriers addressed
  - Electrochemical Energy Storage
    - ❖ Performance → Beyond Li-ion
    - ❖ Life → Cycling performance
    - ❖ Abuse tolerance → Dendrite prevention

Budget

- Total Funding:
  - DOE share: $890K
  - Contractor share: $99K
- Funding for FY 18:
  - DOE share: $297K
  - Contractor share: $33K

Partners

- Theoretical calculations computed on:
  - NERSC
  - CFN

  computing systems.

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Relevance - Objectives

❑ Overall objectives

❖ High-throughput framework to screen materials

- Identify promising solid electrolytes
  - Study interfacial stability of Li-metal/solid electrolytes

❖ Study 'dendrite'-resistant electrolyte

- Understand the underlying science controlling the propagation of dendrites in ionic conductors
- Develop a model and criteria to identify promising solid electrolyte materials that can prevent dendrite propagation.

❑ Objectives this period

- ❖ Electrolyte material conductivity screening
- ❖ Theoretical-numerical model of lithium propagation in defects and interface evolution during deposition.

Relevance – Impact

- Li metal anodes with solid electrolytes greatly increases energy density and safety of current batteries.
- Improve understanding of complex evolution of Li-metal / solid electrolyte interfaces during electrochemical cycling
- Develop theoretical means to quantify and asses potential Li-metal propagation and battery failure mechanisms
- Determine design principles to develop reliable all solid-state batteries for beyond Li-ion technology.

Milestones FY2019

Milestone	Month/Year	Status
❖ Li conductivity screening using ab initio molecular dynamics and nudged elastic band method to screen for materials with high Li-mobility.	September 2018	Completed
❖ Development of critical criteria controlling dendrite propagation	January 2019	Completed
❖ Evaluation of bulk elastic properties	March 2019	Completed
❖ Adapt fracture models that describe crack propagation in materials to Li-dendrite propagation	June 2019	Ongoing

Milestones FY2020

Milestone	Month/Year	Status
❖ Asses electronic conductivity of candidate/promising SE materials	September 2019	On target
❖ Develop theoretical and numerical implementation of network deposition stress field and fracture	January 2020	On target
❖ Determine critical material properties and mesoscale composition necessary to prevent Li metal propagation.	March 2020	On target

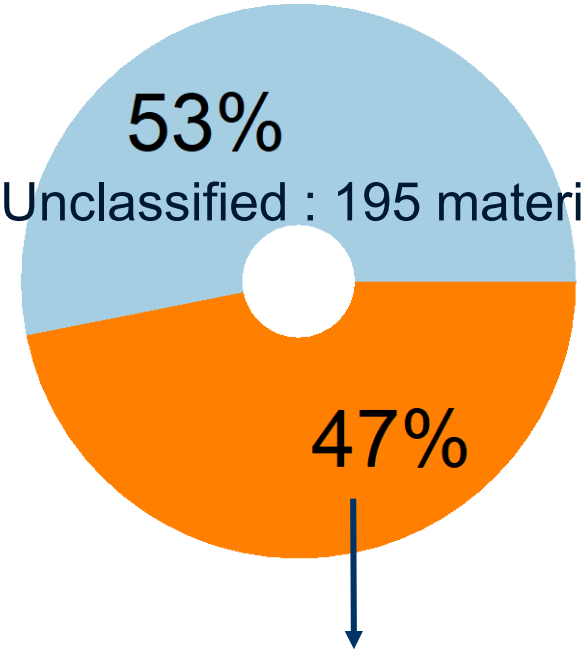
Approach 1

- High-throughput ab-initio modeling to develop stable high-conducting solids that protect Li metal. Search for anion arrangements that lead to good Li-ion transport. Then evaluate chemistries for them that have good electrochemical stability

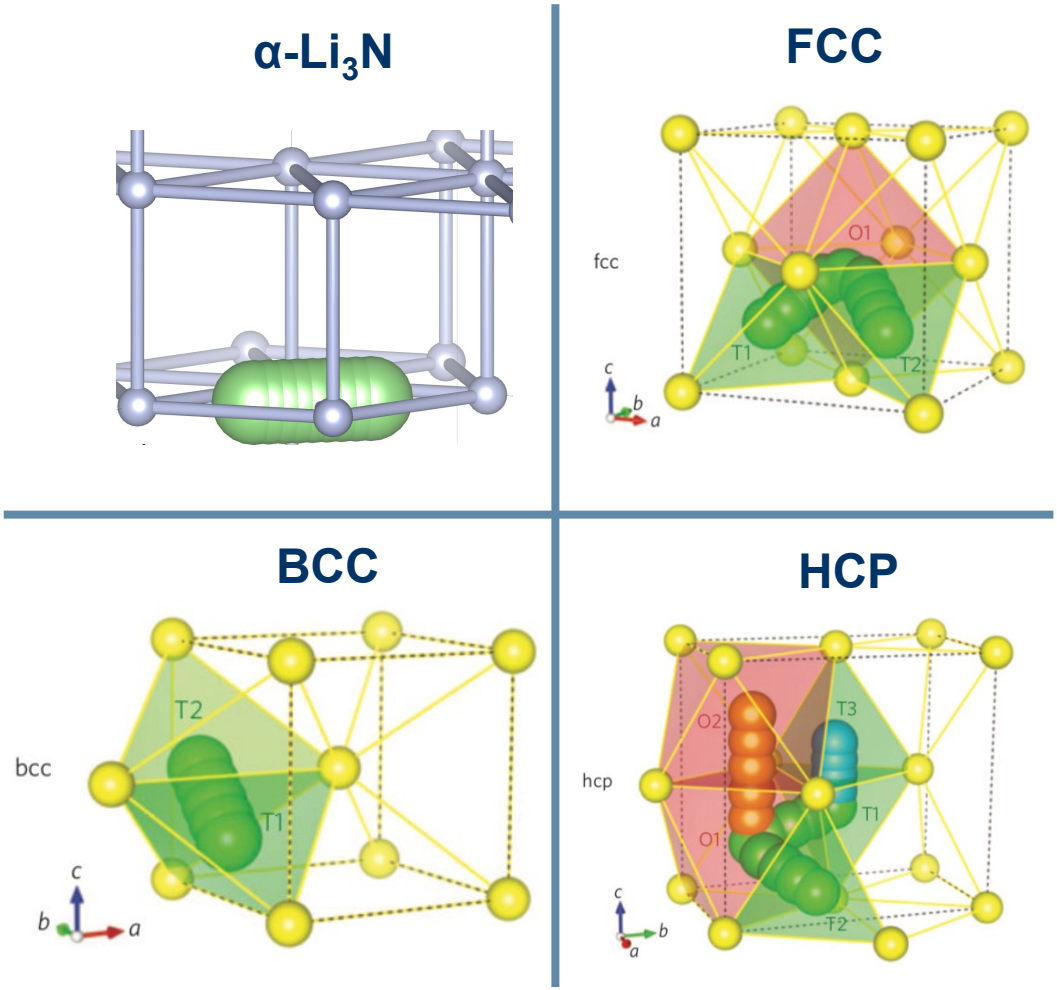
- Continuum modeling theory for Li-metal penetration through the solid conductor. Systematically evaluate various possible mechanism by which Li-metal can penetrate a conductor (chemical, stress concentration, flow-induced pressure, electron transport).

Approach 2 - First Principle Calculation of Activation Barriers for Li hopping in Prototype Anion Frameworks

Li-Nitrides in ICSD Database



- α-Li_3N : 50
- FCC : 107
- BCC : 23
- HCP : 32



Classification of Li-nitrides into structural prototypes

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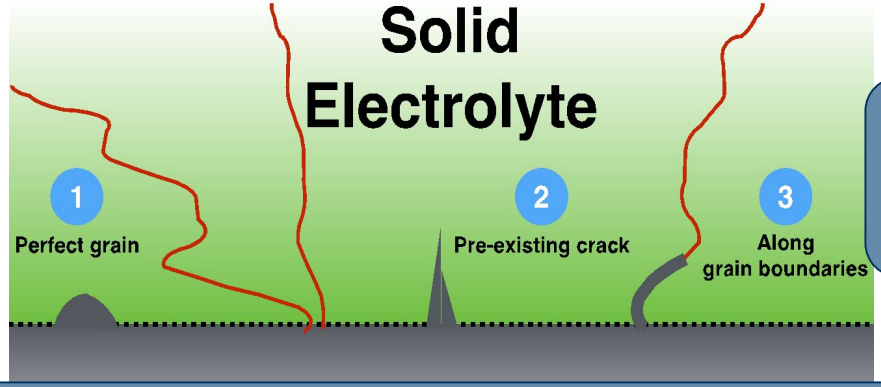
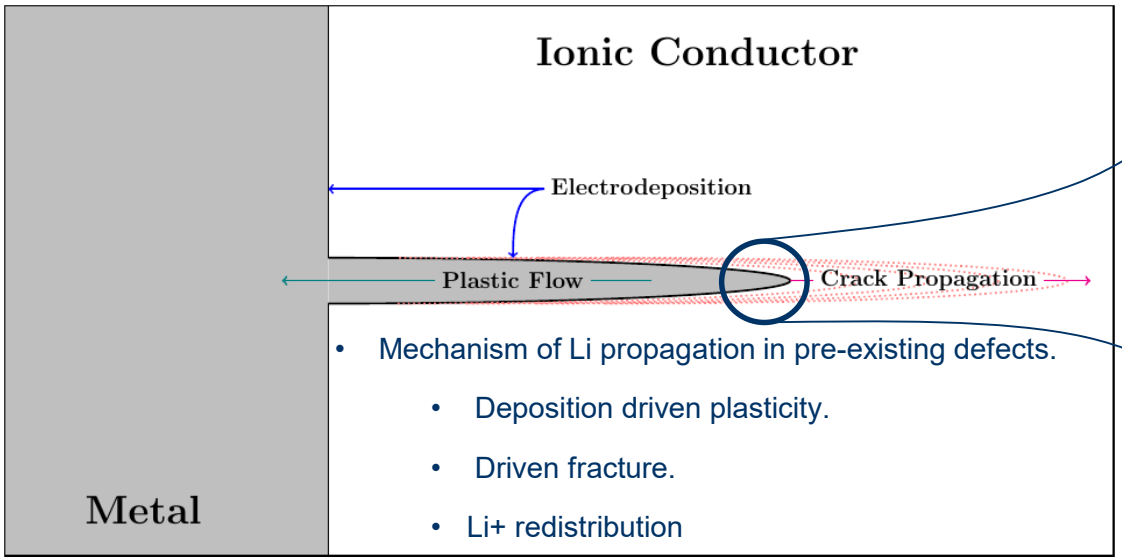
Approach 3 – Continuum Theory on Dendrite Formation and Propagation in SSB



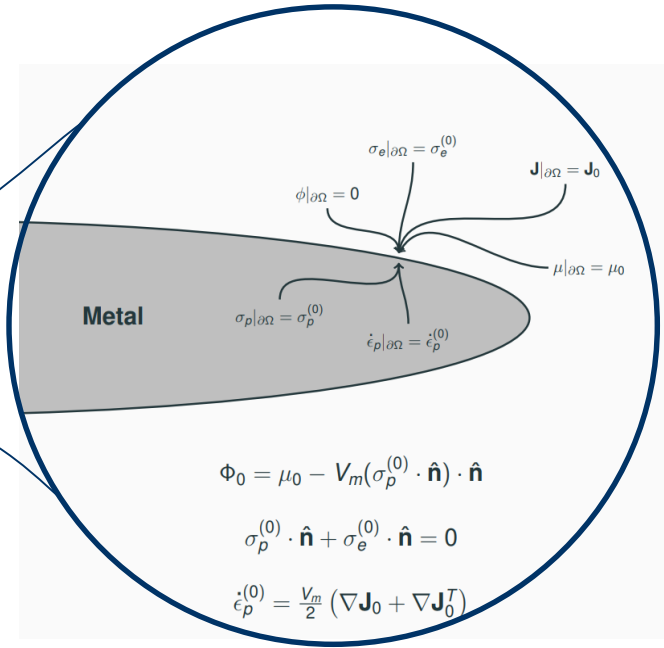
* In single mobile ion inorganic conductors, electroneutrality ↔ zero ion concentration gradient.

Region	Equations
Conductor bulk	$\Phi = RT\ln\bar{a} + RT\ln\left(\frac{c}{c_T - c}\right) + zF\phi - \beta\Omega_v(\boldsymbol{\sigma}_e : \boldsymbol{\epsilon}_e)$
	$\boldsymbol{J} = -M\left(\frac{c_T}{c_T - c}\nabla c + \frac{zFc}{RT}\nabla\phi - \frac{\beta\Omega_v c}{RT}\nabla(\boldsymbol{\sigma}_e : \boldsymbol{\epsilon}_e)\right)$
	$\boldsymbol{\sigma}_e = -\frac{Y\nu}{(1+\nu)(1-2\nu)}tr(\boldsymbol{\epsilon}_e)\mathbb{I} + \frac{Y}{1-\nu}\boldsymbol{\epsilon}_e$
	$\nabla\cdot\boldsymbol{J} = 0$
	$\nabla\cdot\boldsymbol{\sigma}_e = 0$
Metal bulk	$\boldsymbol{\sigma}_p = -P\mathbb{I} + 2\eta\dot{\boldsymbol{\epsilon}}_p$
	$-\nabla P + \nabla\cdot\eta\boldsymbol{\epsilon}_p = 0$
Interface	$\Phi_0 = \mu_0 - V_m(\boldsymbol{\sigma}_p^{(0)}\cdot\hat{\boldsymbol{n}})\cdot\hat{\boldsymbol{n}}$
	$\dot{\boldsymbol{\epsilon}}_p^{(0)} = \frac{V_m}{2}\left(\nabla\boldsymbol{J}_0 + \nabla\boldsymbol{J}_0^T\right)$
	$\boldsymbol{\sigma}_p^{(0)}\cdot\hat{\boldsymbol{n}} + \boldsymbol{\sigma}_e^{(0)}\cdot\hat{\boldsymbol{n}} = 0$

- Mechanism of dendrite nucleation (Model a).
- Mechanism of dendrite growth and crack propagation (Model b).
- Mechanism of dendrite propagation along grain boundary (Model c).

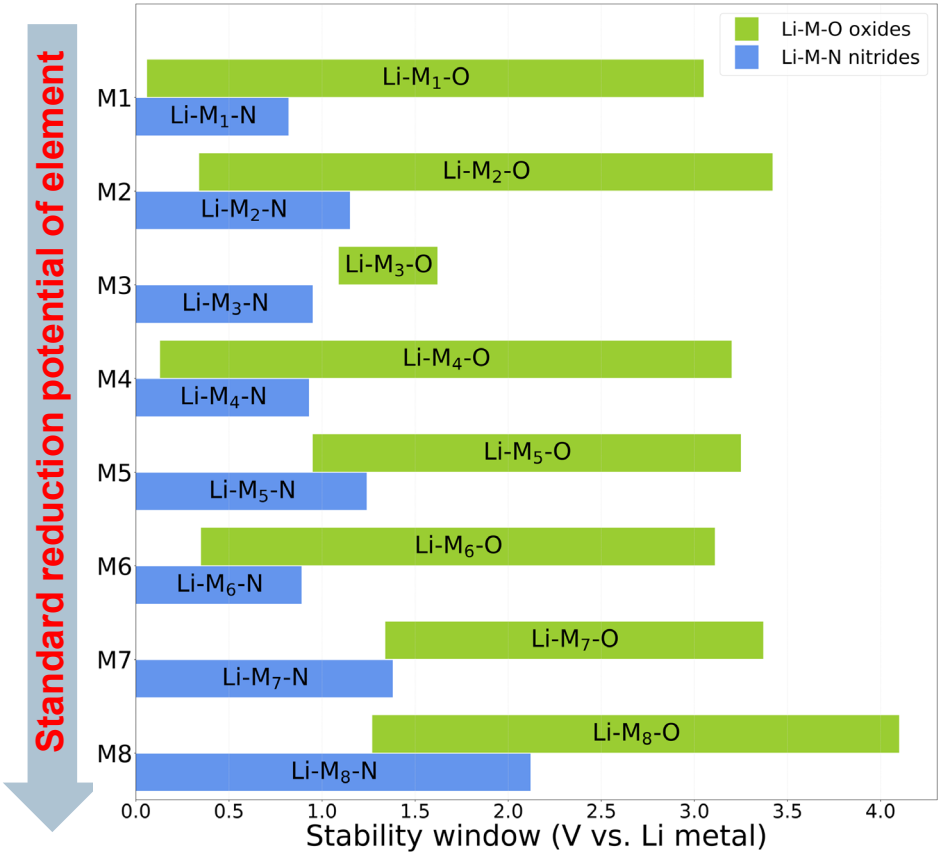


- Mechanism of Li propagation in pre-existing defects.
  - Deposition driven plasticity.
  - Driven fracture.
  - Li+ redistribution



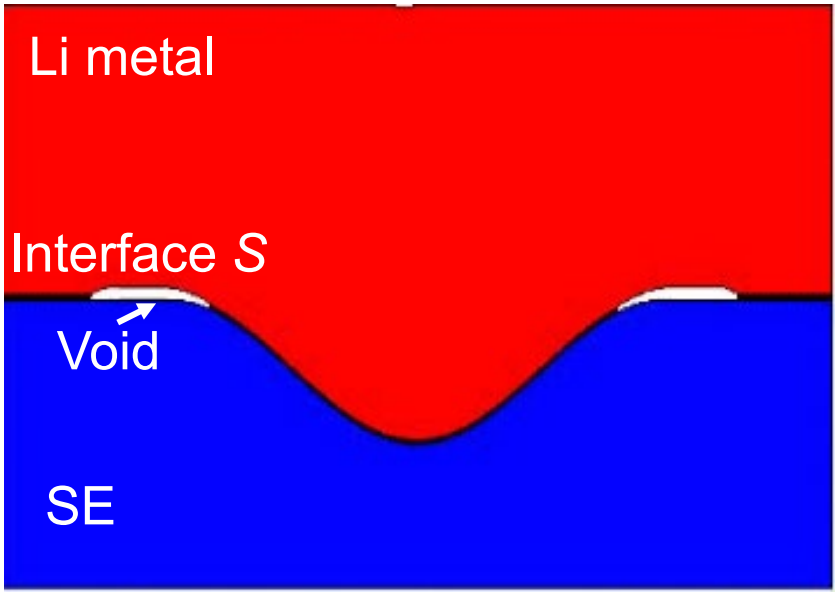
Previous Accomplishments –

- Electrochemical stability against Li metal



- For the same element M in Li-M-X (X=O or N) ternaries, nitrides exhibit better stability against Li-metal than their oxide counterparts.

- Inhomogeneous Deposition of Li at Interface

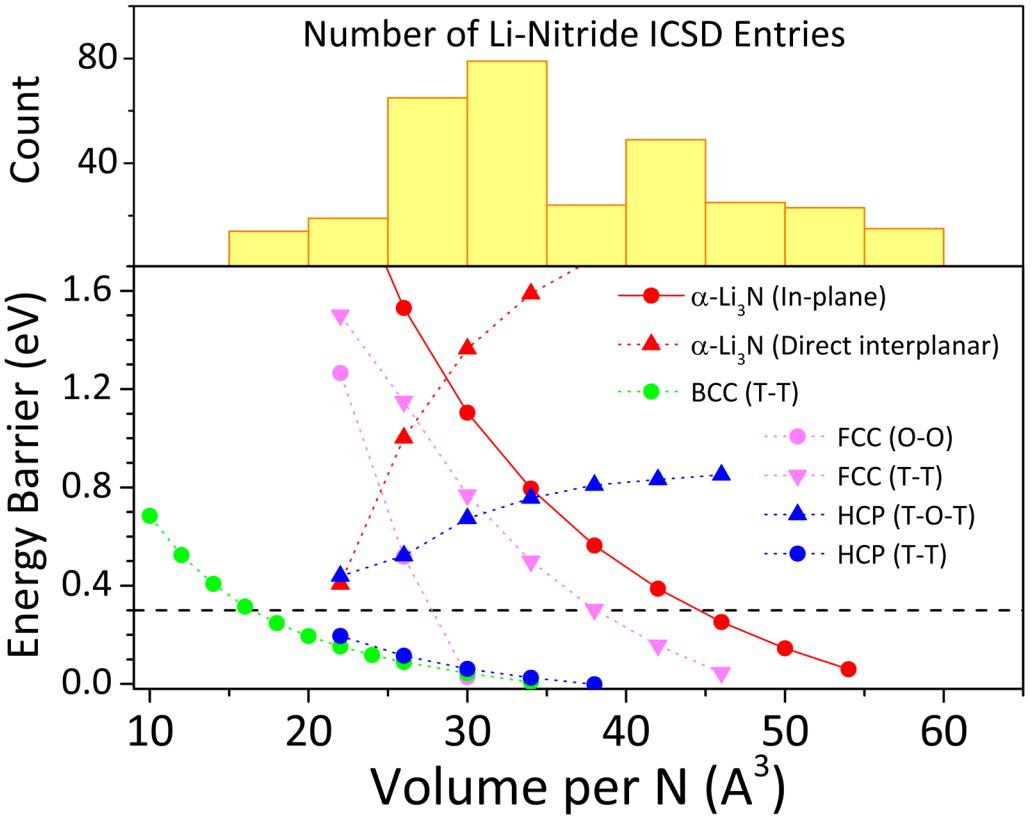


- Inhomogeneous deposition on rough surface of solid electrolyte leads to contact loss and dendrite formation.

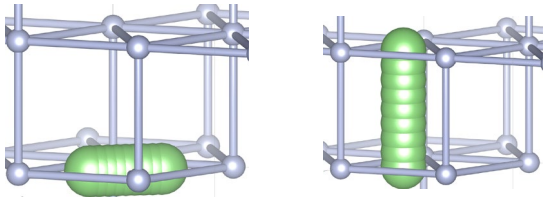
Accomplishments 1 – Nitrides with structural advantage for conductivity

❑ Potential Li-ion Nitride conductors

- ❖ Calculation of energy barriers in prototypes for various volume to achieve 0.3 eV or lower barrier
- ❖ BCC anion packings tend to have low barrier energy for a given volume.
- ❖ A substantial number of structures exists within the desired volume range.



In-plane hop **Direct interplanar hop**



α-Li_3N Hops

Within desirable volume range: likely good conductors

17 α-Li_3N type
19 FCC types
24 HCP types
21 BCC types

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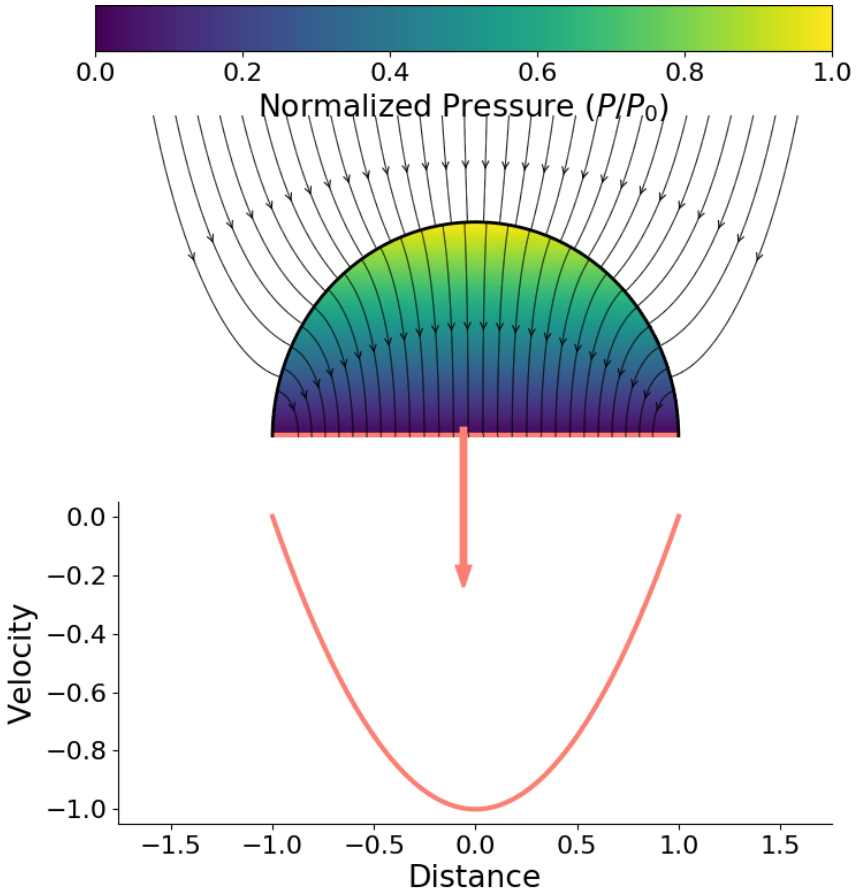
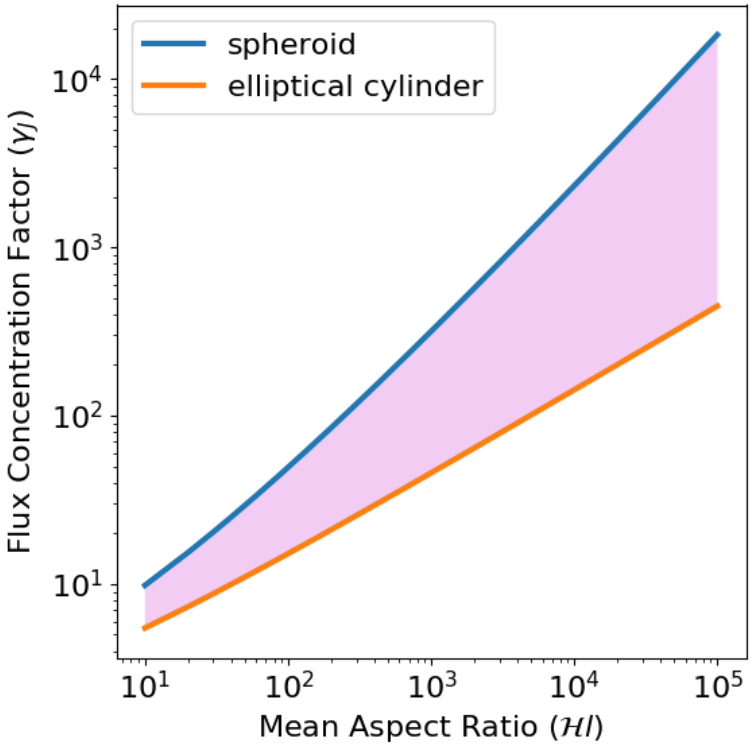
Accomplishments 2 – Investigation of current inhomogeneity and mechanical effects near surface imperfections

- **Hydrostatic Stress Distribution at Defect Tips**



Li-metal flow velocity profile is analogous to fully developed viscous channel flow

- **Current Density Concentration at Sharp Defects**



Field focusing effects at sharp interfaces translates to inhomogeneous current density, which in turn gives rise to shear stress and plastic flow of Li metal.

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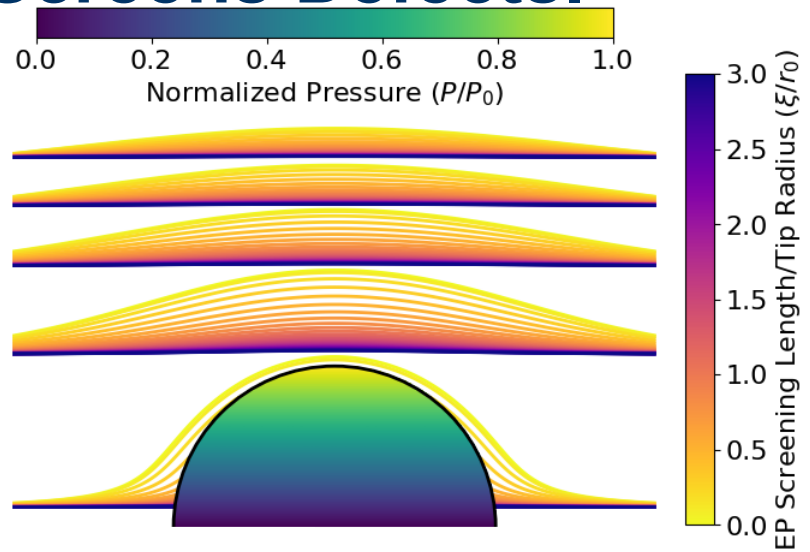
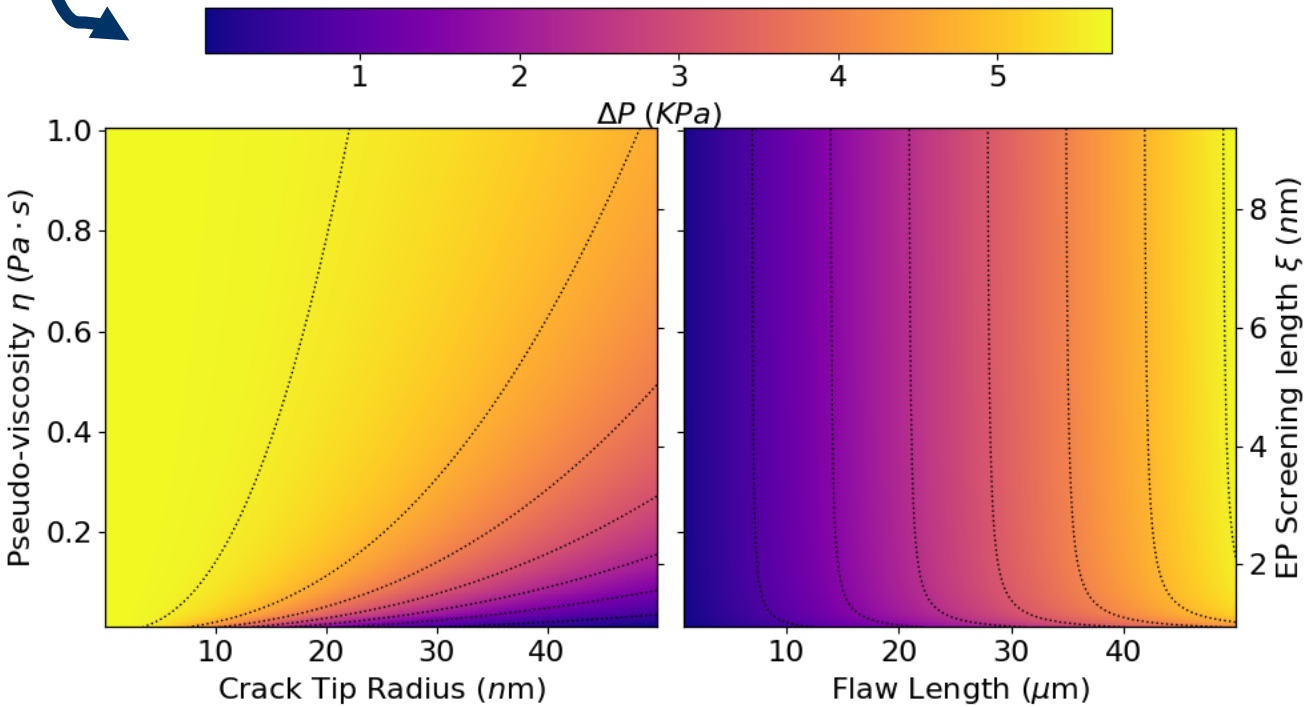
Accomplishments 3 – Increased Pressure Drives Li+ Redistribution & Screens Defects.

- Inhomogeneous stress field causes Li+ redistribution.
- Defects effectively screened by pressure effects on Li+ diffusion potential.

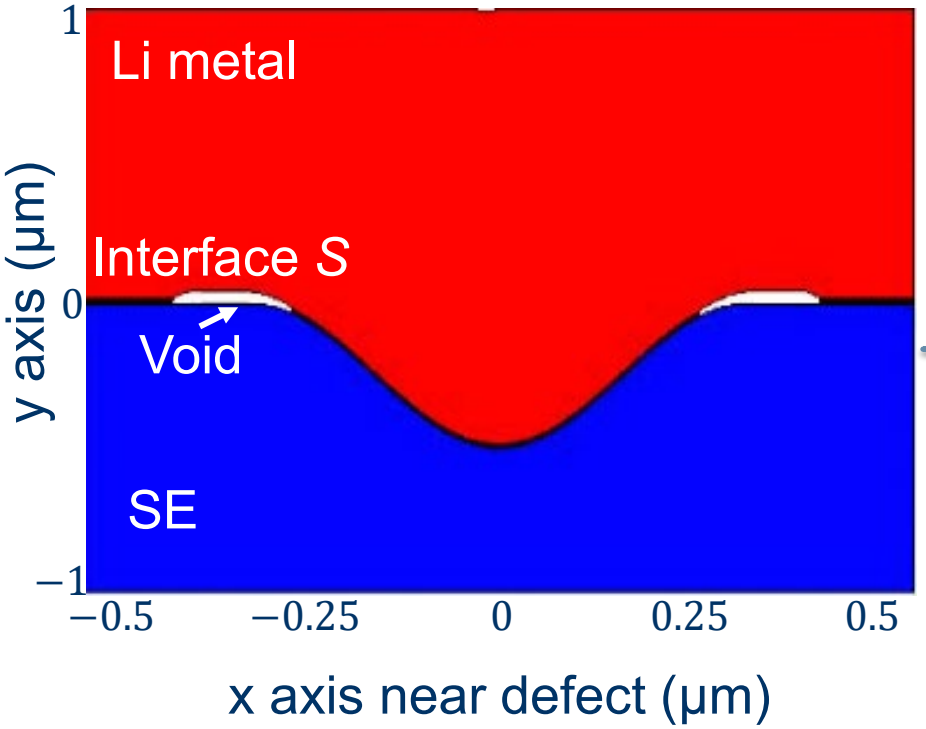




- Fracture driven by deposition at a single defect is not possible!

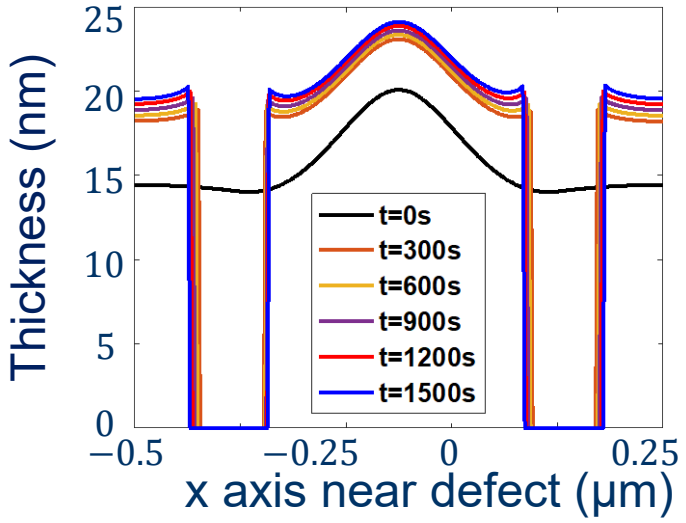
Accomplishments 4 – Inhomogeneous Deposition of Li at Interface

❑ Li Deposition

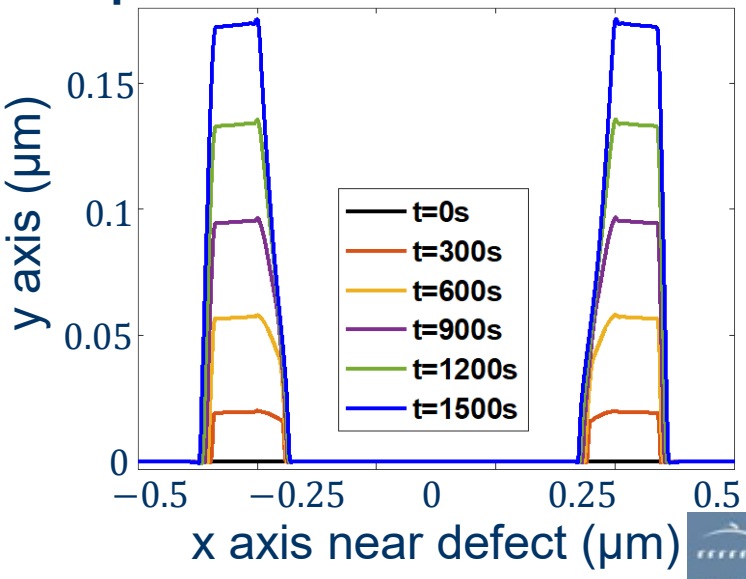


❖ Inhomogeneous deposition on rough surface of solid electrolyte leads to contact loss

❖ **Deposition at Anode Surface**



❖ **Gap at Interface**



Partners and Collaborations

Most Calculations are done using the following national computing resource:

- National Energy Research Scientific Computing Center (NERSC) based at the Lawrence Berkeley National Laboratory;
- Center for Functional Nanomaterials (CFN) at Brookhaven National Laboratory and Argonne National Laboratory

Responses to Reviewers' Comments

- No previous year comments for this project.

Remaining Challenges and Barriers

- **Effects of non-zero electronic conductivity in electrolytes**
  - Non-negligible electronic conductivity in electrolyte can lead to different deposition scenarios, such as disconnected Li-metal regions..
  - Partially connected Li metal in addition to electronically conductive phases can create electric short.

- **Fracture caused by bulk stress fields**
  - Multiple deposition sites in porous, grain boundary and defect networks give rise to bulk stress fields.
  - Bulk stress fields can concentrated at tips, edges, defects and give rise to *classical* brittle fracture.

Proposed Future Research

- **Task 1: Electronic Conductivity Screening**
  - Asses electronic conductivity of obtained SE materials
- **Task 2: Bulk Stress Field Theoretical Model**
  - Develop theoretical and numerical implementation of network deposition stress field and fracture
- **Task 3: Design Criteria for Stable/Safe Cycling SSBs**
  - Determine critical material properties and mesoscale composition necessary to prevent Li metal propagation

Conclusions

Candidate Solid Electrolytes

- Screened solid electrolytes through large-scale material recognition based on ICSD and materials prediction.
- Based on previous results on chemical stability, further screening from ionic conductivity calculations was done to obtain promising electrolyte materials.

Dendrite Formation and Propagation

- Theoretical analysis of deposition and Li-metal propagation at defects via induced plasticity and ceramic fracture.
- Increased pressure from current density focusing at defects can be screened out by Li redistribution from coupled pressure diffusion potential.
- High pressing pressure, smoothed interface, fast Li^+ migration in solid electrolyte and slow charge transfer of Li/Li^+ reaction will be helpful on reducing interfacial contact loss.

Summary

Relevance

- Interfacial stability of Li-metal/solid electrolytes.
- Improve lack of understanding of Li deposition and interface dynamics in advanced batteries.
- Design principles to develop reliable all solid-state batteries

Approach

- First Principle Calculation on Chemical Stability
- Nudged Elastic Band (NEB) used for energy barriers calculation
- Continuum Theory on Dendrite Formation and Propagation in SSB

Technical accomplishments

- Ionic conductivity screening of superionic Nitride conductors with low energy barriers and high chemical stability vs Li.
- Upper bound calculation of current density concentration at sharp defects gives ~100x increase for sharpest flaws expected.
- Inhomogeneities in current density give rise to shear stresses that lead to Li metal plastic flow and hydrostatic pressure gradients along defects.
- Inhomogeneous current density can be reduced by increasing Li+ conductivity.

Proposed future research

- Effects of electronic conductivity in solid electrolyte materials.
- Bulk stress fields and fracture from microstructural effects on bulk deposition